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(54) ETHYLENE-VINYL ALCOHOL COPOLYMER WATER-BASED COMPOSITION EXCELLENT IN BARRIER PROPERTY**(57)Abstract:**

PROBLEM TO BE SOLVED: To obtain an ethylene-vinyl alcohol copolymer water-based composition having high barrier property and excellent in stability to leaving and in bending resistance of its film.

SOLUTION: This composition is characterized by including (A) an ethylene- vinyl alcohol copolymer having 16-70 mol% ethylene content and (B) an ethylene- vinyl alcohol copolymer having 2-15 mol% ethylene content and dispersing the ethylene-vinyl alcohol copolymer (A) in a state of microparticles into water and dissolving the ethylene-vinyl alcohol copolymer (B) in water.

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CLAIMS

[Claim(s)]

[Claim 1]It consists of 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer and (A), the ethylene content 2 - 15-mol% of an ethylene-vinylalcohol copolymer (B), An ethylene-vinylalcohol copolymer aqueous composition, wherein an ethylene-vinylalcohol copolymer (A) distributes by the shape of a particle underwater and an ethylene-vinylalcohol copolymer (B) is dissolving in water.

[Claim 2]The aqueous composition according to claim 1 which is a denaturation ethylene-vinylalcohol copolymer (a1) in which 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer (A) has an ionic group of the ethylene content 16 - not less than 80% of the degree of 70-mol % and saponification.

[Claim 3]An ethylene-vinylalcohol copolymer (A) The ethylene content 16 - 70-mol %, The aqueous composition according to claim 1 which consists of an ethylene-vinylalcohol copolymer (a2) which does not contain denaturation ethylene-vinylalcohol copolymer (a1) and 16-70 mol of ethylene content% of ionic group which has an ionic group of not less than 80% of the degree of saponification.

[Claim 4]The aqueous composition according to any one of claims 1 to 3 which contains the ethylene content 2 - 15-mol% of ethylene-vinylalcohol copolymers [0.05-100 copies of] (B) to 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer (A)100 weight section.

[Claim 5]As opposed to 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer and (A), the ethylene content 2 - total weight 100 weight section of 15-mol% of an ethylene-vinylalcohol copolymer (B), The aqueous composition according to any one of claims 1 to 4 which carries out 60-1500 weight-section content of the water.

[Claim 6]A multilayer-structure object which applies the aqueous composition according to any one of claims 1 to 5, and has a layer to dry further at least.

[Claim 7]A manufacturing method of the aqueous composition according to any one of claims 1 to 5 adding solution of the ethylene content 2 - 15-mol% of an ethylene-vinylalcohol copolymer (B) to aqueous dispersion liquid of 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer (A).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the ethylene-vinylalcohol copolymer aqueous composition which has high barrier property and was excellent in leaving stability and the flexibility of a coat.

[0002]

[Description of the Prior Art]The ethylene-vinylalcohol copolymer (it may be hereafter written as EVOH) produced by saponifying an ethylene-vinyl ester copolymer, especially an ethylene-vinylacetate copolymer, Since it excels in barrier property, such as oxygen, or oil resistance and chemical resistance, it is observed as charges of protective covering material, such as a wrapping raw material, a plastic-molding thing, a surface of metal, paper, wood.

[0003]Advanced barrier property is demanded in the film for food packing for which antioxidizing of contents or maintenance of a scent is needed especially, a sheet, laminated material, a hollow container, etc. The vinyl chloride wallpaper, vinyl chloride leather, and sheet which consist of elasticity VCM/PVC require the covering material which prevents the bleeding of a plasticizer. Then, filling highly barrier property, a smell retaining property and an oilproof, and medicine-proof performance is carried out widely.

[0004]As a method of generally forming an EVOH layer, the method by melt molding or injection molding, the method of laminating an EVOH film, etc. are enforced widely. On the other hand, the solution and aqueosity dispersion liquid of EVOH are applied and the method of drying is proposed. This method attracts attention from the ability of a coat to be easily formed also in the thing of complicated shape, such as that a coat with comparatively thin thickness can be formed, and a hollow container.

[0005]By the method of applying the solution of EVOH, the solution of high concentration being fundamentally difficult to use it for hyperviscosity and a solvent However, for organic solvents, such as dimethyl sulfoxide, or the partially aromatic solvent of a lot of alcohol and water, There are problems, such as a also economically disadvantageous thing -- in the coat morphosis, the device for aggravation of the work environment by vaporization of an organic solvent and recovery of an organic solvent is needed. On the other hand, it is thought that the method of applying the aqueosity dispersion liquid of EVOH is advantageous from the work environment of the above [a solvent] in a drainage system or a point of economical efficiency, and it is expected.

[0006]The usual surface-active agent or the usual polymers protective colloid as aqueosity dispersion liquid of EVOH, For example, although what carried out emulsification dispersion under coexistence of

polyethylene oxide, carboxymethyl cellulose, hydroxymethylcellulose, polyvinyl alcohol, etc. is proposed by JP,54-101844,A, JP,56-61430,A, etc., The aqueosity dispersion liquid of EVOH which has recent years still higher leaving stability were called for. As for the multilayer-structure object which applies the aqueosity dispersion liquid of EVOH shown above, and is acquired by drying, the tendency for flexibility and barrier property to fall easily was seen.

[0007]Although the aqueosity dispersion liquid using the denaturation EVOH which has an ionic group as dispersion stabilizer are indicated to JP,5-86240,A and JP,5-93009,A, The room of improvement was left behind about the flexibility and barrier property of the multilayer-structure object which apply the leaving stability of these aqueosity dispersion liquid, and these aqueosity dispersion liquid, and are produced by drying.

[0008]

[Problem(s) to be Solved by the Invention]This invention provides the ethylene-vinylalcohol copolymer aqueous composition which has high barrier property and was excellent in leaving stability and the flexibility of a coat.

[0009]

[Means for Solving the Problem]An aforementioned problem consists of 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer and (A), the ethylene content 2 - 15-mol% of an ethylene-vinylalcohol copolymer (B), An ethylene-vinylalcohol copolymer (A) distributes by the shape of a particle underwater, and it is attained by providing an ethylene-vinylalcohol copolymer aqueous composition, wherein an ethylene-vinylalcohol copolymer (B) is dissolving in water.

[0010]In a suitable embodiment, 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer (A) consists of a denaturation ethylene-vinylalcohol copolymer (a1) which has an ionic group of not less than 80% of the degree of saponification the ethylene content 16 - 70-mol%. In a suitable embodiment, 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer (A) The ethylene content 16 - 70-mol %, It consists of an ethylene-vinylalcohol copolymer (a2) which does not contain denaturation ethylene-vinylalcohol copolymer (a1) and 16-70 mol of ethylene content% of ionic group which has an ionic group of not less than 80% of the degree of saponification.

[0011]In a suitable embodiment, aqueosity dispersion liquid of 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer (A), A denaturation ethylene-vinylalcohol copolymer (a1) which has an ionic group of not less than 80% of the degree of 16-70 mol of ethylene content % and saponification is made into dispersion stabilizer, Let an ethylene-vinylalcohol copolymer (a2) which does not contain 16-70 mol of ethylene content% of ionic group be a dispersoid.

[0012]In a suitable embodiment, an aqueous composition of this invention contains the ethylene content 2 - 15-mol% of ethylene-vinylalcohol copolymers [0.05-100 copies of] (B) to 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer (A)100 weight section.

[0013]In a suitable embodiment, an aqueous composition of this invention, 60-1500 weight-section content of the water is carried out to 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer and (A), the ethylene content 2 - total weight 100 weight section of 15-mol% of an ethylene-vinylalcohol copolymer (B).

[0014]In a suitable embodiment, an aqueous composition of this invention is applied to a substrate etc., and it dries and it is used as a multilayer-structure object.

[0015] This invention, It is related with a manufacturing method of the aqueous composition according to any one of claims 1 to 4 adding solution of the ethylene content 2 - 15-mol% of an ethylene-vinylalcohol copolymer (B) to aqueous dispersion liquid of 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer (A).

[0016] This invention relates to a stabilization method of the ethylene content 16 by addition of 2-15 mol of ethylene content% of ethylene-vinylalcohol copolymer (B) - aqueous dispersion liquid of 70-mol% of an ethylene-vinylalcohol copolymer (A).

[0017]

[Embodiment of the Invention] The aqueous composition of this invention consists of 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer and (A), the ethylene content 2 - 15-mol% of an ethylene-vinylalcohol copolymer (B), An ethylene-vinylalcohol copolymer (A) distributes by the shape of a particle underwater, and the ethylene-vinylalcohol copolymer (B) is dissolving in water. That is, EVOH (A) exists underwater as what is called a dispersoid, and dissolves EVOH (B) underwater as a solute.

[0018] Although what is produced by saponifying an ethylene-vinyl ester copolymer as 16-70 mol of ethylene content% of an ethylene-vinylalcohol copolymer (A) used for this invention is preferred and vinyl acetate is preferred especially as vinyl ester which carries out copolymerization to ethylene, Other fatty acid vinyl ester (vinyl propionate, vinyl pivalate, etc.) can also be used together. EVOH can contain 0.0002-0.2 mol of vinyl silane compound % as a copolymer component. Here, as a vinylsilane system compound, vinyltrimetoxysilane, vinyltriethoxysilane, BINIRUTORI (beta-methoxy-ethoxy) Silang, and gamma-metacryloxy propyl methoxysilane are mentioned, for example. Especially, vinyltrimetoxysilane and vinyltriethoxysilane are used suitably.

[0019] The ethylene contents of 16-70 mol of ethylene content% of EVOH (A) used for this invention are 17 - 65-mol % suitably. From a viewpoint of obtaining the molded product excellent in barrier property, the 18-60-mol thing which is % of an ethylene content is more suitably preferred. Some which there is a possibility that an ethylene content may become what has the stability of aqueous dispersion liquid with less than [15 mol % / insufficient], and exceed 70-mol % have a possibility of becoming what has dissatisfied barrier property. The degree of saponification of a vinyl ester ingredient is not less than 80% preferably, and is not less than 99% still more preferably not less than 95% more preferably from a viewpoint of obtaining the molded product excellent in barrier property. When an ethylene content exceeds 70-mol %, there is a possibility that barrier property may run short. There is a possibility that barrier property and moisture resistance may worsen in less than 80% in the degree of saponification.

[0020] In a suitable embodiment, 16-70 mol of ethylene content% of EVOH (A) consists of the denaturation EVOH which has an ionic group. From a viewpoint of the barrier property of a coat, and flexibility which consists of an aqueous composition of this invention. 16-70 mol of ethylene content% of EVOH (A) The ethylene content 16 - 70-mol %, Especially the thing consisted of EVOH (a2) which does not have the denaturation EVOH (a1), and 16-70 mol of ethylene content% of ionic group which have an ionic group of not less than 80% of the degree of saponification is preferred, and the embodiment which makes ** (a1) dispersion stabilizer and makes ** (a2) a dispersoid is still more preferred.

[0021] The ionic group of the denaturation EVOH (a1) which is used by this invention and which has an ionic group of not less than 80% of the degree of 16-70 mol of ethylene content % and saponification includes the basis which dissociates underwater and shows ionicity, i.e., an anionic group, a cationic

group, and a both sexes group. From a point of a dispersion stability-ized effect, an anionic group is preferred.

[0022]As an anionic group, bases, such as sulfonic acid, a sulfonate, sulfate ester, sulfuric ester salt, phosphoric acid, an phosphate, carboxylic acid, and carboxylate, may be mentioned, and these acid and salts may be contained simultaneously. Sulfonic acid, a sulfonate, carboxylic acid, and carboxylate are preferred at the point that the dispersion stability-ized effect is excellent, and especially sulfonic acid and/or a sulfonate salt are desirable.

[0023]As a cationic group, bases, such as amine and its salt, quarternary ammonium salt, phosphonium salt, and sulfonium salt, are mentioned. A dispersion stability-ized effect has especially greatly preferred quarternary ammonium salt. As a both sexes group, aminocarboxylate (betaine type), an aminosulfonic acid salt (sulfobetaine type), amino sulfuric ester salt (sulfate betaine type), etc. are mentioned.

[0024]Although a block or a graft copolymer of what is called a thing into which the ionic group was introduced at random, and an EVOH ingredient and the ingredient which has an ionic group, etc. is illustrated about the structure of the denaturation EVOH (a1), From a viewpoint of the stability of aqueous dispersion liquid, the denaturation EVOH into which the ionic group was introduced at random is used suitably.

[0025]Although the manufacturing method in particular of the denaturation EVOH with which the ionic group was introduced at random is not limited, For example, radical copolymerization of the monomer containing an ionic group is carried out to ethylene and vinyl ester, Subsequently, the method of saponifying the vinyl ester unit in the obtained copolymer, and changing into a vinyl alcohol unit, After carrying out the addition reaction of the ionic group component to the method of making add an ionic group component to EVOH polymer, and introducing into it, or an ethylene-vinyl ester copolymer, the method of saponifying the vinyl ester unit in this copolymer, and changing into a vinyl alcohol unit, etc. are mentioned. The method of carrying out radical copolymerization of the monomer containing an ionic group to ethylene and vinyl ester, saponifying the vinyl ester unit in the copolymer subsequently obtained, and changing into a vinyl alcohol unit especially, is preferred. Methods, such as the polymerization, saponification, and an addition reaction, can be enforced by a publicly known method.

[0026]Although it is as copolymerizable as ethylene, such as formic acid vinyl, vinyl acetate, vinyl propionate, benzoic acid vinyl, vinyl acetate trifluoride, and vinyl pivalate, and a monomer convertible into vinyl alcohol can be used by saponifying this copolymer as vinyl ester, Especially vinyl acetate is preferred.

[0027]As an ionic group content monomer which carries out copolymerization to ethylene and vinyl ester, the thing which has a basis convertible into an ionic group or an ionic group and in which radical homopolymerization or radical copolymerization is possible can be used. The example is shown below.

[0028]As an anionic group content monomer sulfonate anion nature group content monomer, The acrylamide system sulfonate monomer like 2-(meta) acrylamide 2-methylpropanesulfonic acid sodium (meta), The styrene system sulfonate monomer like styrene-sulfonic-acid potassium, The allyl system sulfonate monomer like sodium allylsulfonate and the vinylsulfonates like sodium vinylsulfonate or these ammonium salt monomers, these acid monomers, etc. are mentioned. It is usable when ester of these sulfonic acid also changes after-polymerization ester into the salt or acid.

[0029]As a carboxylic acid anion nature group content monomer, mono- ** JI, such as acrylic acid,

methacrylic acid, a maleic anhydride, itaconic acid, and fumaric acid, a polycarboxylic acid system vinyl monomer, its alkali metal salt, ammonium salt, etc. are mentioned. Such ester species can also change after-polymerization ester into a salt, and it is usable.

[0030]The amino group content (meta) acrylamide system monomer like cationic group content monomer aminopropyl acrylamide or methacrylamide, Aminoethyl acrylate, the amino group content (meta) Acre rate like methacrylate, or its salt of polymerization nature is also good, and preferred. Especially the 4th class salt of the of coloring of polymer is also preferred few. For example, they are trimethyl acrylamide propyl ammoniumchloride, a triethyl METAKUOIRU ethylammonium star's picture, etc.

[0031]These monomers can also be used [also using it alone and] together. Copolymerization with the monomer of others [the range which does not check a dispersion stability-ized effect] is also possible.

[0032]Although the content of an ionic group is suitably chosen by within the limits with a dispersion stability-ized effect, 0.05-50-mol % is desirable from a point of a dispersion stability-ized effect to the EVOH component unit under this denaturation EVOH (a1). It is still more preferably [further 0.2-15 mol % and also 0.2-10 mol% of] desirable 0.1-30-mol%. Less than [0.05 mol %], there is a possibility that a dispersion stability-ized effect may become small and the thing exceeding 50-mol % has a possibility that the water resisting property of the coat produced by applying and drying aquosity dispersion liquid and barrier property may become insufficient.

[0033]Including other units which do not contain an ionic group during the denaturation EVOH (a1) in the range which does not spoil a dispersion stability-ized effect substantially does not interfere.

[0034]The ethylene content of the presentation of the EVOH ingredient under denaturation EVOH (a1) needs to be more than 80% (the degree of saponification said by this invention shows the degree of saponification of a vinyl ester unit) of the degree of 16-70-mol % and saponification. the suitable range of an ethylene content -- more than 16 mol % -- further -- desirable -- more than 17 mol % -- further -- it is more than 18 mol %. About a maximum, it is less than 60 mol % suitably for a 65 mol % less or equal and a pan suitably. From a viewpoint of the barrier property of a coat, not less than 90%, the desirable degree of saponification is not less than 95% more preferably, is not less than 97% still more preferably, and is not less than 99% especially preferably.

[0035]Although the degree of polymerization of the denaturation EVOH (a1) does not have restriction in particular, 100 or more are desirable from a point of a dispersion stability-ized effect. Although the maximum of a degree of polymerization does not have restrictions in particular, it is preferred that a degree of polymerization (a1) uses 2000 or less thing from a viewpoint [control the superfluous increase in solution viscosity and] of obtaining good dispersion performance. The degree of polymerization of the denaturation EVOH is searched for here from the intrinsic viscosity measured at 30 ** among the water / phenol system partially aromatic solvent containing 1 mol/l. of ammonium thiocyanate (weight ratios 15/85).

[0036]EVOH (a2) which does not contain the ionic group of not less than 80% of the degree of saponification is used as a dispersoid of the aqueous composition of this invention in the suitable embodiment 16-70 mol of ethylene content% used for this invention as above-mentioned. Although what is produced by saponifying an ethylene-vinyl ester copolymer as this EVOH (a2) is preferred and vinyl acetate is preferred especially as vinyl ester which carries out copolymerization to ethylene, Other fatty acid vinyl ester (vinyl propionate, vinyl pivalate, etc.) can also be used together. EVOH can contain 0.0002-

0.2 mol of vinyl silane compound % as a copolymer component. Here, as a vinylsilane system compound, vinyltrimetoxysilane, vinyltriethoxysilane, BINIRUTORI (beta-methoxy-ethoxy) Silang, and gamma-metacryloxy propyl methoxysilane are mentioned, for example. Especially, vinyltrimetoxysilane and vinyltriethoxysilane are used suitably.

[0037]The ethylene content of the above-mentioned EVOH (a2) used for this invention has suitably preferred 17-65-mol thing which is % and is 18-60-mol % more suitably. Some which there is a possibility that an ethylene content may become what has the stability of aqueous dispersion liquid with less than [15 mol % / insufficient], and exceed 70-mol % have a possibility of becoming what has dissatisfied barrier property. The degree of saponification of a vinyl ester ingredient is not less than 80% preferably, and is not less than 99% especially preferably not less than 97% still more preferably not less than 95% more preferably from a viewpoint of obtaining the molded product excellent in barrier property. There is a possibility that barrier property and moisture resistance may worsen in less than 80% in the degree of saponification.

[0038]As near the thing of the ethylene content and the degree of saponification of EVOH (a2) which do not contain the ionic group of not less than 80% of the degree of 16-70 mol of ethylene content % and saponification as the ethylene content of the above-mentioned denaturation EVOH (a1) and the degree of saponification is desirable in respect of a particle dispersion stability-ized effect. It is preferred that the absolute value of the difference of the ethylene content of EVOH (a2) and the denaturation EVOH (a1) is less than 10 mol %, it is less than 7 mol % more preferably, is less than 5 mol % still more preferably, and, specifically, is less than 1 mol % especially preferably. Similarly, as for the absolute value of the difference of the degree of saponification of the point of a particle dispersion stability-ized effect to EVOH (a2), and the denaturation EVOH (a1), it is preferred that it is 5% or less, it is more preferred that it is 3% or less, and it is still more preferred that it is 1% or less.

[0039]16-70 mol of ethylene content% of EVOH of this invention (A) has especially a preferred thing consisted of EVOH (a2) which does not have the denaturation EVOH (a1) and the ethylene content 16 which have an ionic group of the ethylene content 16 - not less than 80% of the degree of 70-mol % and saponification - 70-mol% of an ionic group. Although ** (a1) and the content in particular of (a2) are not limited, it is preferred that the above-mentioned EVOH (A) consists of 1 (a1) to 99 % of the weight and (a2) 1 to 99 % of the weight, and it is more preferred to consist of 5 (a1) to 95 % of the weight and (a2) 5 to 95 % of the weight.

[0040]Since what has an extremely low degree of polymerization of EVOH (a2) which does not contain the ionic group of not less than 80% of the degree of 16-70 mol of ethylene content % and saponification does not have the low preferred intensity of a formation coat, 600 or more things are usually used preferably 300 or more. It is advantageous to carry out spreading use as aqueous dispersion liquid as what has a high degree of polymerization, and it can usually be used to about 5000 thing. The degree of polymerization of a dispersoid is searched for here from the intrinsic viscosity measured at 30 ** among water / phenol system partially aromatic solvent (weight ratios 15/85). Copolymerization of the copolymerizable monomers other than ethylene and vinyl ester may be carried out at less than 5 mol % if needed.

[0041]Although the manufacturing method in particular of the aqueous composition of this invention is not limited, the manufacturing method which adds the solution of the ethylene content 2 - 15-mol% of an ethylene-vinylalcohol copolymer (B) to the aqueous dispersion liquid of 16-70 mol of ethylene content% of

ethylene-vinylalcohol copolymer (A), It is desirable especially from a viewpoint of simple nature and the leaving stability of the aqueous composition obtained.

[0042]The manufacturing method in particular of the aqueous dispersion liquid of 16-70 mol of ethylene content% of EVOH (A) is not limited, but conventionally publicly known methods, such as JP,54-78748,A, JP,54-101844,A, and JP,5-179001,A, are adopted suitably.

[0043]There is no restriction in particular in the manufacturing method of the aqueous dispersion liquid of EVOH (A) which distributes EVOH (a2) which similarly does not contain the ionic group which is a dispersoid by making denaturation EVOH (a1) into dispersion stabilizer, and it is usable in a publicly known method. Contact the solution of EVOH (a2) which is a dispersoid under the water which is the nonsolvent of EVOH, and churning under coexistence of the denaturation EVOH (a1) which is dispersion stabilizer, and EVOH particles For example, 3 micrometers or less, Aqueous dispersion liquid can be obtained by making it deposit as a particle of 1 micrometer or less the optimal, and subsequently removing 2 micrometers or less of solvents preferably. The path of particles is number average particle diameter here.

[0044]As a solvent, for example Methyl alcohol, ethyl alcohol, propyl alcohol, Dihydric alcohol, such as monohydric alcohol, such as butyl alcohol, ethylene glycol, and propylene glycol, Phenols, such as trihydric alcohol, such as glycerin, phenol, and cresol, In two or more sorts, these hydrated compounds can use amines, such as ethylenediamine and trimethylene diamine, dimethyl sulfoxide, dimethylacetamide, N-methyl pyrrolidone, etc., independent or being mixed. Especially desirable solvents are the partially aromatic solvent of a water-alcohol system, for example, water-methyl alcohol, water-normal propyl alcohol, water-isopropyl alcohol, etc.

[0045]Although the denaturation EVOH (a1) can be made to live together in the inside of the solution of EVOH (a2) which is a dispersoid, or underwater [of nonsolvent] or its both, it is desirable to make it live together in the solution of EVOH (a2) preferably. The organic solvent in a solvent is removable by proper methods, such as an evaporation method, an extraction method, or dialysis. Although the high thing of the grade of removal is desirable, the organic solvent of a small rate may be made to remain on balance with economical efficiency.

[0046]As an option, at an elevated temperature, although EVOH dissolves, if low temperature is used, after carrying out the heating and dissolving of EVOH (a2) of a dispersoid, and the denaturation EVOH of dispersion stabilizer (a1) to the solvent which becomes insoluble, the method of carrying out deposit distribution as particles is also employable by cooling the solution. It can be considered as aqueous dispersion liquid by replacing the solvent by water after an appropriate time. As a solvent which dissolves at an elevated temperature and deposits at low temperature, a partially aromatic solvent with independent or the water of alcohols, etc. can be used among the solvents shown previously.

[0047]or [contacting as an option the solution of EVOH (a2) which made the denaturation EVOH (a1) live together to nonsolvent furthermore] -- or the method of filtering the particles which carried out deposit distribution and distributing the particle underwater under coexistence of the denaturation EVOH (a1) is also possible by cooling.

[0048]Also in these manufacturing methods, EVOH (a2) of a dispersoid, and the denaturation EVOH of dispersion stabilizer (a1). Dissolve at the bottom of churning, and the temperature of 50-75 °C in these common solvents, for example, the partially aromatic solvent of water-alcohol, and it is considered as a solution, Subsequently, by cooling (temperature-10-30 °C), depositing, decentralizing EVOH particles

(emulsion-izing), removing alcohol under decompression next (the temperature of 10-30 **, the pressure 10 - 150mmHg), and carrying out desired quantity removal of the water further, Especially the method of obtaining the aqueous dispersion liquid of desired solids concentration is preferred.

[0049]Although there is no restriction in particular in the moisture content of the aqueous dispersion liquid of 16-70 mol of ethylene content% of EVOH (A), It is preferred that the maximum of the content of water is 1000 or less weight sections to EVOH(A)100 weight section, it is more preferred that they are 600 or less weight sections, and it is still more preferred that they are 400 or less weight sections. As for the minimum of the content of water, it is preferred that they are 60 or more weight sections, it is preferred that they are 80 or more weight sections, and it is preferred that they are 100 or more weight sections.

[0050]2-15 mol of ethylene content% of ethylene-vinylalcohol copolymer (EVOH) (B) used for this invention, Although what is produced by saponifying an ethylene-vinyl ester copolymer like 16-70 mol of ethylene content% of ethylene-vinylalcohol copolymer (A) is preferred and vinyl acetate is preferred especially as vinyl ester which carries out copolymerization to ethylene, Other fatty acid vinyl ester (vinyl propionate, vinyl pivalate, etc.) can also be used together. EVOH can contain 0.0002-0.2 mol of vinyl silane compound % as a copolymer component. Here, as a vinylsilane system compound, vinyltrimethoxysilane, vinyltriethoxysilane, BINIRUTORI (beta-methoxy-ethoxy) Silane, and gamma-metacryloxy propyl methoxysilane are mentioned, for example. Especially, vinyltrimethoxysilane and vinyltriethoxysilane are used suitably.

[0051]The minimum of the ethylene content of 2-15 mol of ethylene content% of EVOH (B) is more than 3 mol % preferably, and is more than 5 mol % more preferably. The maximum of an ethylene content is less than 14 mol % preferably, and is less than 13 mol % more preferably. When an ethylene content is less than [2 mol %], as shown in the below-mentioned comparative example 1, the leaving stability of an aqueous composition and flexibility will become dissatisfied. When an ethylene content exceeds 15-mol %, there is a possibility of becoming what has the insufficient water solubility of EVOH (B). When the water solubility of 2-15 mol of ethylene content% of EVOH (B) is insufficient, there is a possibility of having an adverse effect on the ethylene content 16 - the dispersibility of 70-mol% of EVOH (A), and there is a possibility of spoiling the leaving stability of the aqueous composition of this invention.

[0052]As for the minimum of the degree of saponification of 2-15 mol of ethylene content% of EVOH (B), it is preferred that it is not less than 70% from a viewpoint of obtaining high barrier property. The minimum of the degree of saponification is not less than 80% more preferably, and is more than 85 mol % especially preferably. Although there is no restriction in particular in the maximum of the degree of saponification and it is substantially usable also in the thing of 100% of the degree of saponification, it is preferred from a water-soluble viewpoint of 2-15 mol of ethylene content% of EVOH (B) that the maximum of the degree of saponification is 99% or less. Since the crystallinity of EVOH (B) tends to become high easily when the degree of saponification exceeds 99%, there is a possibility that water solubility may become dissatisfied.

[0053]Although the degree of polymerization in particular of 2-15 mol of ethylene content% of EVOH (B) is not limited, from a viewpoint of the leaving stability of the aqueous composition of this invention, and the flexibility of the coat which consists of aqueous compositions, as for the minimum of a degree of polymerization, it is preferred that it is 100 or more, and it is 150 or more more preferably. From a viewpoint of acquiring sufficient water solubility, as for the maximum of the degree of polymerization of this EVOH (B), it is preferred that it is 2000 or less, it is more preferred that it is 1500 or less, it is still more preferred

that it is 1000 or less, and it is preferred that it is especially 700 or less. The degree of polymerization of this EVOH (B) is searched for here from underwater and the intrinsic viscosity measured at 30 °C.

[0054] It consists of 16-70 mol of ethylene content% of EVOH (A), the ethylene content 2 - 15-mol% of EVOH (B), EVOH (A) distributes by the shape of a particle underwater, and the method in particular of obtaining an aqueous composition, wherein EVOH (B) is dissolving in water is not limited. For example, the method of adding EVOH (B) of dryness to the aqueous dispersion liquid of EVOH (A), This EVOH (B) is dissolved in the partially aromatic solvent of water and alcohol (methanol, ethanol, propanol, etc.), Dissolve EVOH (B) in the method of adding to the aqueous dispersion liquid of EVOH (A), or water, and it is considered as solution, When producing the method, the ethylene content 16 - the aqueous dispersion liquid of 70-mol% of EVOH (A) which add this solution to the aqueous dispersion liquid of EVOH (A), the ethylene content 2 - 15-mol% of EVOH (B) are taught together, and the method of obtaining an aqueous composition, etc. are mentioned. Contrary to the above-mentioned method, it is usable also in the method of adding the aqueous dispersion liquid of EVOH (A) to the dry matter or solution of EVOH (B).

[0055] Also in these, as above-mentioned, from a viewpoint of simple nature and the leaving stability of the aqueous composition obtained. The method of dissolving 2-15 mol of ethylene content% of EVOH (B) in water, considering it as solution, and adding this solution to the aqueous dispersion liquid of EVOH (A) is preferred, and the method of adding under stirring of the aqueous dispersion liquid of EVOH (A) especially is preferred.

[0056] Although the aqueous composition of this invention consists of 16-70 mol of ethylene content% of EVOH (A) and (B), the ethylene content 2 - 15-mol% of EVOH (B), It is preferred that the blending ratio of EVOH (A) and EVOH (B) is [EVOH (B)] 0.05 - 100 weight section to EVOH(A) 100 weight section. The minimum of the blending ratio of EVOH (B) is 0.1 or more weight sections to EVOH(A) 100 weight section more suitably, is 0.5 or more weight sections still more suitably, is one or more weight sections especially suitably, and is five or more weight sections the optimal. The minimum of the blending ratio of EVOH (B) is 90 or less weight sections to EVOH(A) 100 weight section more suitably, is 80 or less weight sections still more suitably, is 50 or less weight sections especially suitably, and is 30 or less weight sections the optimal. When the loadings of EVOH (B) are less than 0.05 weight sections to EVOH(A) 100 weight section, there is a possibility that the improvement effect of the flexibility of the coat which consists of the leaving stability of an aqueous composition and the aqueous composition of this invention may become insufficient. When the loadings of EVOH (B) exceed 100 weight sections to EVOH(A) 100 weight section, there is a possibility that the improvement effect of the leaving stability of the aqueous composition of this invention may become insufficient, and there is a possibility of becoming what has the insufficient water resisting property of the coat which consists of aqueous compositions and barrier property.

[0057] As for the moisture content of the aqueous composition of this invention, it is preferred to carry out 60-1500 weight-section content of the water to total weight 100 weight section of EVOH (A) and EVOH (B). The minimum of the content of water is 70 or more weight sections more preferably, is 80 or more weight sections still more preferably, and is 100 or more weight sections especially preferably. The maximum of the content of water is 1000 or less weight sections more preferably, is 800 or less weight sections still more preferably, and is 600 or less weight sections especially preferably. When the content of water exceeds 1500 weight sections, there is a possibility that the time which the desiccation at the time of applying this aqueous composition to a substrate etc. takes may become long. When the content of water

is less than 60 weight sections, there is a possibility that the leaving stability of an aqueous composition may become insufficient.

[0058]To the aqueous composition of this invention, viscosity the making it fall purpose Sodium hydroxide, It is arbitrary to add alkaline earth metal compounds, such as alkali metal compounds, such as sodium chloride, sodium acetate, sodium sulfate, and sodium nitrate, calcium hydroxide, a calcium chloride, calcium acetate, calcium sulfate, and a calcium nitrate, and other electrolytes. Although the content in particular is not limited, it is preferred to carry out 0.01-0.5 weight-section combination to 16-70 mol of ethylene content% of EVOH and (A), the ethylene content 2 - total weight 100 weight section of 15-mol% of EVOH (B).

[0059]employing the outstanding dynamic performance and chemical performance efficiently, although the aqueous composition obtained by the method of this invention is useful as an application material which forms the coat of the outstanding barrier property -- other uses -- for example, spray desiccation is carried out, and it can be made particle powder and can use for large areas, such as a binder, a vehicle, etc. of a paint or adhesives.

[0060]It is possible to add a usual surface-active agent and protective colloid in the aqueous composition of this invention in the range which does not bar the purpose of this invention if needed. It is also possible to add stabilizer, paints, lubricant, an antifungal agent, or a film formation auxiliary agent to other aqueous dispersion liquid, lights, or heat of resin, etc.

[0061]As explained above, the aqueous composition of high solids concentration which was excellent in the stability at the time of storage or use according to this invention is obtained, And since it is aqueous, there is an advantage which problems, such as environmental contamination, do not have, either, and it can apply to the various substrate surface as useful paint which can form the thin coat which is excellent in barrier property, a smell retaining property, an oilproof and chemical resistance, and flexibility outstanding by spreading desiccation. here -- as a substrate -- especially -- thermoplastics {polyolefine (polyethylene.) Polyester, such as polypropylene, polyamide, polyvinyl chloride, A polyvinylidene chloride, polycarbonate, polystyrene, polyvinyl alcohol, the various mold goods (a film.) which consist of vinyl acetate resin (ethylene-vinylacetate copolymer etc.)) etc. It is raised as what has a suitable sheet, a cup, a bottle, etc., and fiber aggregates (paper, a nonwoven fabric, textile fabrics, a fibrous casing, etc.), inorganic substances (cement etc.), metal, the wallpaper made of polyvinyl chloride resin, the photographic printing paper, etc. are raised.

[0062]As a method of applying the aqueous composition of this invention to a base material surface, arbitrary means, such as the regurgitation from a casting head, a roll coat, a doctor roll coat, a doctor knife coat, a curtain flow coat, a spray, immersion, and brush coating, are illustrated. As a method of drying and heat-treating the substrate applied in this way, a dry-heat-treatment method, for example, an infrared irradiation method, a hot-air-drying method, etc. are illustrated. Such infrared irradiation, hot air drying, etc. may be used alone, respectively, and can also be used together. As for the temperature of desiccation and heat treatment, it is preferred that it is 30-180 **, it is preferred about a lower limit, and is not less than 80 ** the optimal. [of not less than 50 **] The time of desiccation and heat treatment is 1 to 5 minutes desirable still more suitably [5 seconds - 10 minutes]. It is free during desiccation / heat treatment to make conditions, for example, temperature, fluctuate, for example, at first, process at low temperature and raise temperature gradually. The coat which was excellent in barrier property is formed in a base material

surface by performing such desiccation and heat treatment.

[0063] In a base material surface, spreading desiccation, i.e., carry out an anchor coat, is preferred beforehand in adhesives by a dry lamination process etc. As adhesives for dry laminations, especially if **** adhesive strength is enough, it will not be limited. For example, the adhesives for dry laminates of a polyurethane system and a polyester system are mentioned. Corona treatment, sputtering processing, high frequency processing, flame treatment, chromate treatment, a solvent etching process, etc. and the surface treatment that combined these may be performed to a base material surface.

[0064] It is 2-6 micrometers that the thickness of spreading, desiccation, and the coat after heat-treating is [1-10-micrometer] 0.5-15 micrometers about the aqueous composition of this invention the optimal desirable still more suitably.

[0065] There is no restriction in particular also about the composition of the layered product containing the coat formative layer which consists of a substrate furthermore obtained with the described method, and an aqueous composition of this invention, and it can laminate by a publicly known method conventionally, and can be further made a multilayer. For example, an extrusion lamination process, a dry lamination process, etc. are mentioned as these methods.

[0066] The usual method of laminating on both sides of the layer of adhesive resin is adopted as correlation in these lamination. although limitation in particular is not carried out as adhesive resin -- unsaturated carboxylic acid or its anhydride -- an olefin system polymer (for example, polyethylene.) The denaturation olefin system polymer containing the carboxyl group produced by combining with the copolymer which makes polyolefines, such as polypropylene and polybutene, and an olefin a subject chemically (for example, an addition reaction, a grafting reaction) is mentioned. Specifically Maleic anhydride graft modified polyethylene, maleic anhydride graft denaturation polypropylene, One sort or two sorts of mixtures chosen from the maleic anhydride graft denaturation ethylene-ethyl acrylate copolymer and the maleic anhydride graft denaturation ethylene-vinylacetate copolymer are mentioned. Denaturation olefin system polymers, such as a glycidyl group, alkoxysilane groups, etc., such as a polymerization nature unsaturated compound which has glycidyl groups, such as glycidyl acrylate and glycidyl methacrylate, and a polymerization nature unsaturated compound which has a methacryloxy-propyl-trimethoxysilane group, are mentioned. Two or more these functional groups may be combined. Specifically Glycidyl modified polyethylene, glycidyl denaturation polypropylene, A glycidyl denaturation ethylene-ethyl acrylate copolymer, a glycidyl denaturation ethylene-vinylacetate copolymer, One sort or two sorts of mixtures chosen from alkoxysilane modified polyethylene, alkoxysilane denaturation polypropylene, and an alkoxysilane denaturation ethylene-vinylacetate copolymer are mentioned. In addition, the polyester system resin which made the constituent polyvalent carboxylic acid, polyhydric alcohol, and hydroxycarboxylic acid is also mentioned as adhesive resin. When adopting the dry laminate method, the same adhesives for dry laminates as the above-mentioned can be used, and it is not limited in particular.

[0067] The containers (a bag, a cup, a tube, a tray, a bottle, etc.) which comprise these layered products (a film, a sheet, etc.) manufactured by these methods are very preferred as the object for general food packing, and an object for packaging of medical products.

[0068]

[Example] Although an example explains this invention concretely below, this invention is not limited only to the following examples. A weight ratio shows a solvent presentation. The item measured in the example

was measured as follows.

[0069]It measured with light scattering measurement using <mean particle diameter of aqueous dispersion liquid of EVOH (A)> Otsuka Electronics Co., Ltd. make laser F-potential meter ELS-8000.

[0070]The <leaving stability> aqueous composition was neglected for ten days at 20 **. The viscosity before and behind neglect was measured in the Brookfield viscometer.

[0071]It is a biaxially oriented polypropylene film (20 micrometers of thickness) as a <oxygen transmission quantity> substrate. What applied the urethane system anchor coat agent (Oriental Morton AD335 A/Cat-10) to the priming side of Tokyo Cellophane paper was used, and it applied by the air knife coat method, and it dried and heat-treated for 5 minutes, and 110 ** of multilayer films of coat thickness 2mmicro were obtained. After neglecting the multilayer film produced above for 14 days under 20 **-85%RH and controlling the humidity of it enough, OX-TRAN 10/50A of Modern Control was used, and it measured by 20 ** of measuring condition-85%RH.

[0072]A <flexibility> Gelboflex tester (made by physical science industrial incorporated company) is used, The multilayer film produced by the above which was neglected for 14 days under 20 **-65%RH, and was cut into 12 inches x 8 inches Cylindrical shape 3.5 inches in diameter, and nothing, Both ends were grasped, 440 twists of an angle were added at 3.5 inches of the initial grasping interval of 7 inches, the grasping interval of 1 inch at the time of the maximum crookedness, and the beginning of a stroke, and 2.5 inches of after that repeated the operation which is a straight-line horizontal movement under the condition of 20 ** and 65%RH with the speed for /40 times. After repeating this reciprocation 100 times, oxygen transmission quantity was measured by the method mentioned above in 20 **-85%RH, and the ratio of the oxygen transmission quantity before and behind crookedness showed flexibility.
(Flexibility) =(oxygen transmission quantity after crookedness)/(oxygen transmission quantity before crookedness)

[0073]The 1g right balance of the <moisture content of aqueous composition> aqueous composition was carried out, and the weight (Z (g)) of what dried at 105 ** for 1 hour, and was made only into solid content was measured. The moisture contents of an aqueous composition are 16-70 mol of ethylene content% of EVOH and (A), the ethylene content 2 - the content of water to total weight 100 weight section of 15-mol% of EVOH (B), and were computed by the following formulas.

Moisture content (weight section) = $100 \times (1-Z)/Z$ of an aqueous composition [0074]example 12-acrylamide 2-methylpropanesulfonic acid sodium receives EVOH -- 0.3-mol % -- 32 mol of ethylene content % by which random copolymerization was carried out. The partially aromatic solvent solution of water/methyl alcohol =50/50 which contains the denaturation EVOH (a1) which has an ionic group of the degree % and the degree of polymerization 800 of 99.6 mol of saponification 10% of the weight was prepared. Addition mixing of this partially aromatic solvent solution 50 weight section was carried out at EVOH(a2)28 weight section, 100 copies of methyl alcohol, and 100 copies of water of the degree % and the degree of polymerization 1000 of 99.5 mol of 32 mol of ethylene content % and saponification, and the heating stirring dissolution was carried out at 65 **.

[0075]When this solution was cooled to 10 ** under churning, particles deposited and stable dispersion liquid were obtained. Mean particle diameter was 0.3 micrometer. Subsequently, decompression evaporation was carried out at 20 ** under churning of these dispersion liquid, methyl alcohol was distilled off, and the aqueous dispersion liquid of EVOH (A) were obtained. The mean particle diameter at this time

received 0.3 micrometer, the moisture content received EVOH(A)100 weight section, and they were 300 weight sections.

[0076]On the other hand, the water which contains the ethylene-vinylalcohol copolymer (B) of the degree % and the degree of polymerization 500 of 98 mol of 5 mol of ethylene content % and saponification 20% of the weight was stirred at 80 **, and the solution of EVOH (B) was obtained. Subsequently, to the aqueous dispersion liquid of EVOH (A) obtained by the above-mentioned method, the solution of above EVOH (B) was added under stirring so that EVOH (B) might become ten weight sections to EVOH(A)100 weight section, and the aqueous composition was obtained. The moisture contents of this aqueous composition were 310 weight sections to total weight 100 weight section of EVOH (A) and EVOH (B). The method shown above estimated the oxygen transmission quantity and flexibility of the tunic which consist of leaving stability of this aqueous composition, and this aqueous composition. An evaluation result is shown in Table 1.

[0077]example 22-acrylamide 2-methylpropanesulfonic acid sodium receives EVOH -- 0.3-mol % -- 32 mol of ethylene content % by which random copolymerization was carried out. The heating stirring dissolution of the partially aromatic solvent solution of water/methyl alcohol =50/50 which contains the denaturation EVOH (a1) which has an ionic group of the degree % and the degree of polymerization 800 of 99.6 mol of saponification 1% of the weight was carried out at 65 **. When this solution was cooled to 10 ** under churning, particles deposited and stable dispersion liquid were obtained. Mean particle diameter was 0.3 micrometer. Subsequently, decompression evaporation was carried out at 20 ** under churning of these dispersion liquid, methyl alcohol was distilled off, and the aqueous dispersion liquid of EVOH (A) were obtained. The mean particle diameter at this time received 0.3 micrometer, the moisture content received EVOH(A)100 weight section, and they were 300 weight sections.

[0078]On the other hand, the water which contains the ethylene-vinylalcohol copolymer of the degree % and the degree of polymerization 300 of 98 mol of 10 mol of ethylene content % and saponification 20% of the weight was stirred at 80 **, and solution was obtained. Subsequently, to the aqueous dispersion liquid of EVOH (A) obtained by the above-mentioned method, the solution of above EVOH (B) was added under stirring so that EVOH (B) might become ten weight sections to EVOH(A)100 weight section, and the aqueous composition was obtained. The moisture contents of this aqueous composition were 310 weight sections to total weight 100 weight section of EVOH (A) and EVOH (B). The method shown above estimated the oxygen transmission quantity and flexibility of the tunic which consist of leaving stability of this aqueous composition, and this aqueous composition. An evaluation result is shown in Table 1.

[0079]The aqueous dispersion liquid of EVOH (A) were produced based on the same technique as comparative example 1 Example 1. Then, the water which contains polyvinyl alcohol of the degree % and the degree of polymerization 1700 of 98 mol of saponification 20% was stirred at 80 **, and solution was obtained. Subsequently, to the above-mentioned EVOH(A) aqueous dispersion liquid, this PVA solution was added under stirring so that polyvinyl alcohol might become ten weight sections to EVOH(A)100 weight section, and the aqueous composition was obtained. The method shown above estimated the oxygen transmission quantity and flexibility of the tunic which consist of leaving stability of this aqueous composition, and this aqueous composition. An evaluation result is shown in Table 1.

[0080]The aqueous dispersion liquid of EVOH (A) were produced based on the same technique as comparative example 2 Example 1. Then, the water which contains the product made from Die Cell

Chemicals and hydroxymethylcellulose 20% was stirred at 40 **, and solution was obtained. Subsequently, to the above-mentioned EVOH(A) aqueous dispersion liquid, this hydroxymethylcellulose solution was added under stirring so that hydroxymethylcellulose might become ten weight sections to EVOH(A)100 weight section, and the aqueous composition was obtained. The method shown above estimated the oxygen transmission quantity and flexibility of the tunic which consist of leaving stability of this aqueous composition, and this aqueous composition. An evaluation result is shown in Table 1.

[0081]The aqueous dispersion liquid of EVOH (A) were produced based on the same technique as comparative example 3 Example 1. Then, the method of showing above the oxygen transmission quantity and flexibility of a tunic which consist of leaving stability and these aqueous dispersion liquid in these aqueous dispersion liquid, without adding anything estimated. An evaluation result is shown in Table 1.

[0082]

[Table 1]

	放置安定性			耐屈曲性		
	放置前 (#1)	放置後 (#1)	比率 (#2)	屈曲前 (#3)	屈曲後 (#3)	比率 (#4)
実施例 1	50	50	1	10	15	1.5
実施例 2	100	150	1.5	15	20	1.3
比較例 1	100	200	2.0	40	400	10
比較例 2	50	100	2.0	500	700	1.4
比較例 3	50	200	4.0	15	200	13

* 1 : 水性組成物の粘度、単位 : poise

* 2 : (放置後の水性組成物の粘度) / (放置前の水性組成物の粘度)

* 3 : 酸素透過量、単位 : $\text{cc} \cdot 2 \mu\text{m} / \text{m}^2 \cdot \text{day} \cdot \text{atm}$

* 4 : (屈曲後の酸素透過量) / (屈曲前の酸素透過量)

[0083]Each aqueous composition of Examples 1 and 2 which have the composition of this invention was excellent in leaving stability, and the coat which consists of this aqueous composition had high barrier property and flexibility. On the other hand, in the comparative example 1 with which the ethylene content of EVOH (B) is not filled to 2-mol%, it became what has insufficient flexibility. In the comparative example 2 which added hydroxymethylcellulose instead of EVOH (B), barrier property fell substantially. It became what has leaving stability with the insufficient comparative example 3 which does not add EVOH (B) at all.

[Effect of the Invention]The ethylene-vinylalcohol copolymer aqueous composition which has high barrier property and was excellent in leaving stability and the flexibility of a coat can be provided.

[Translation done.]